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## TRANSLATION

ON THE PASSIVATION AND CORROSION RESISTANCE  
OF STAINLESS STEEL

By

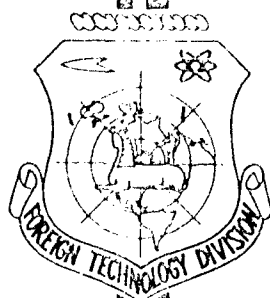
Milan Prazak and Vilem Prazak

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# UNEDITED ROUGH DRAFT TRANSLATION

ON THE PASSIVATION AND CORROSION RESISTANCE  
OF STAINLESS STEEL

BY: Milan Prazak and Vilem Prazak

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## ON THE PASSIVATION AND CORROSION RESISTANCE OF STAINLESS STEEL

by  
Milan Prazak and Vilem Prazak

The possibility of substituting highly alloyed steel with low alloyed. Causes for the resistance to corrosion of stainless steels. Mechanisms of electrochemical passivation. Passivation diagram. Effect of material structure. Experimental part. Discussion of results.

### Introduction

Stainless steel is one of the most desired materials when constructing various technical objects. The universal deficiency of such steel compels the constructor to use it only wherever absolutely necessary; there are cases where it must be replaced by steel or lesser or changed composition of alloying elements. If the need comes up for substituting standard stainless steel we must know the reason and conditions of resistance of this material against corrosion. On the basis of these findings, it is possible to estimate and prepare an alloy, which truly does not attain rapidly the universal corrosion resistance of standard 18-8 steel, but can, at certain closely specified corrosion conditions, have stable resistance.

This report is devoted to the effort of solving the basic problems of the electrochemical corrosion mechanism and to establish corrosion resistance conditions of refined steel with a chromium content.

#### I. Causes of Corrosion Resistance of Stainless Steel

It is known, that the corrosion resistance of stainless steel with a Cr content is indicated by its passivity.\*) Also other metals, e. g., pure iron - are in passive state highly resistant; their passivity is however to a large extent an unstable and it can be attained only by intensified anodic or chemical oxidation.

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\*) Basic data about corrosive effects can be found in book by G. V. Akimov<sup>1)</sup>.

It is typical of stainless steel that it remains spontaneously in passive state in many current corrosion media, just as is the case with chromium.

As a reason for the passive state of metal, the most frequently considered is the existence of a very thin but compact oxide layer, which substantially slows down further oxidation of the metal. On the properties of this layer and its resistance toward the given medium depends the corrosion of passive metal.

The oxide layer originates under the effect of dry air on a majority of metal materials, it now totally stops oxidation - i. e., corrosion under normal temperatures. In a damp medium, e. g., in aqueous solutions the corrosion mechanism is much more unfavorable. The original oxide is destroyed by the solution, the access of oxygen is not sufficient for new passivation and at moderate oxidation of the metal originates at least partially dissolved reaction products, which may get away from the point of their origination, also having no protective properties of the oxide which originated in dry state.

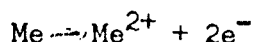
If a passive layer is kept in an aqueous medium, it must be continuously slowly oxidized to compensate for its destroyed places. This process appears as corrosion of the metal in passive state, but in the mentioned materials it is substantially smaller than in metal in active state.

## II. Mechanism of Electrochemical Passivation; Passivation Potential and Critical Passivation Current

The ability of individual metals to form a passive layer during oxidation in an aqueous solution is of various nature and it can be expressed by the magnitude of critical passivation of the current density for given metal and medium. On the polarization curves of basic compounds of stainless steel the meaning of this value can be given (Figure 1).

Iron, chrome and nickel electrode immersed in 1 N  $H_2SO_4$  (i. e., perhaps 5%) without diluted oxygen, remains in active state and has <sup>with/</sup>respect to the solution a definite electrochemical potential, which could not be directly compared with the standard equilibrium potential of these metals. As soon as we force metal electrode

anodic polarization, the potential is more positive than the original currentless potential; electrochemical oxidation and solution of the metal do take place, which are equivalent to the passing current according to the Faraday law. The metal will create its ions of lowest valence, when  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{2+}$  in reaction



The relationship between the potential of the electrode and the passing current is expressed by the polarization curve of given system.

With the rise in positive potential of the electrode, the current corresponding to the solution of the metal also increases; on the other hand, polarization with increasing anodic current is followed by a rise in electrode potential. But after the surpassing of the real passivation potential, there is no further acceleration of this reaction, but conditions are given for a new reaction, at which a passive oxide layer originates. The passivation potential can be obtained with directly defined current (included per unit of area), namely the critical passivation current density. The passivation potential and the critical passivation current density are characteristic values for given metal and medium. After attainment of passive state the passing current drops to a very

small value, corresponding to metal corrosion in passive state; when passivating with forced current, an entirely different reaction will take place, e. g., separation of the oxygen.

The passive layer contains oxides of appurtenant metals in a higher degree,

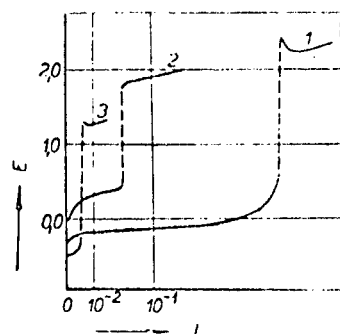


Figure 1. Passivation Curves of Fe 1, Ni 2 and Cr 3 in 1 N  $\text{H}_2\text{SO}_4$  plotted as the dependence of the potential on current density at anodic polarization.

Scales of current density plotted in second square. Parts of curves in negative zone of potential correspond to the dissolvment of the metal in active state, dashed line is the passivation jump for the obtainment of critical passivation of current density. Parts of the curve in positive zone correspond to oxygen separation on passive Fe and Ni and Cr dissolved in transpassive state.

consequently  $\text{Fe}_2\text{O}_3$  will be  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Ni}_2\text{O}_3$  and will have the same fate\*). These oxides are much less soluble and less reactive than oxides of lower degree of oxidation, they also form a typical passive layer. In each oxidation stage of the metal, the oxide is stable only in a definite magnitude of the potential. In the lower boundaries the potential is active: when it passes over in direction of more negative values there will be a reduction in the layer on the unstable dual form and after its solution to the activation of the metal.

The magnitude of the activation potential will for this metal, be in agreement with the passivation potential. The transition between active and passive state is not <sup>at</sup>/all sudden; there is a definite narrow or wider range of the potential, where such a transition does take place, and this is reversible. To this zone corresponds a current drop during passivation and its rise during activation (Figure 2). To grasp (perceive) this curve as combined and reversible (i. e., stable in direction to active zone to passivation and reverse) can be realized in certain instances only by the use of a special measuring device. In these cases when between the current in active and passive state there exists a certain difference and the transition is very steep, the authors<sup>2)</sup> found an incoherent activation and passivation process. It can be proved that this phenomenon is due to internal electric resistance of the measuring system. The difference in values at an activating and passivating potential was also the cause for very slow setting of equilibrium.

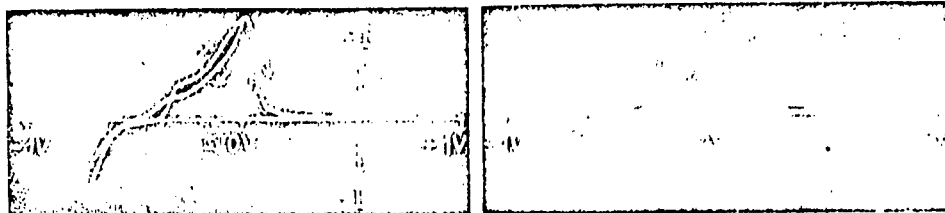
The upper boundary stability potential of the passive layer is the transpassivation potential, i. e., the potential at which trivalent metal oxidizes into highest form, which will create repeatedly soluble ions and lose by it the protective properties.

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\*)  $\text{Ni}_2\text{O}_3$  is also described as a solid  $\text{NiO} + \text{NiO}_2$  solution with staggering composition. The process of the potential during its reduction is the best proof for that. With a variable oxygen composition its properties do change in general.



The values of the passivation (occasionally active) and transpassive potential have a definite relationship with the standard potential of the metal. As is evident from Table 1, these potentials have the most positive values for Ni as electrochemically most refined, while Cr as electrochemically least refined, these potentials have the most negative values.



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Figure 2a, b. Potential Polarization Curves of Cr-Steel with 6.9% Cr.

Curve a - plotted at a rate of potential change  $\frac{dE}{dt} = 0.063$  v/s; curve b - at  $\frac{dE}{dt} = 0.017$  v/s. At a higher rate of registration, it is impossible to establish the equilibrium of the reaction; curve a shows hysteresis and different passivation and activation potentials. In the slowly registered curve b, potentials are almost even.

The passivation potential of Cr lies at considerable negative values, which is one of the causes for its easy passivation.

Table 1.

Tab. I. Přehled pasivačních potenciálů a kritických pasivačních proudů pro některé kovy v 1 N H<sub>2</sub>SO<sub>4</sub>. Potenciály ve vodikové stupnici.

2) Materiál	3) Kritický pasivační proud A/cm <sup>2</sup>	4) Pasivační potenciál V	5) Trans-pasivační potenciál V	6) Standardní potenciál V
Fe	6 · 10 <sup>-1</sup>	+0,50	> +1,9*)	-0,440*)
Ni	5 · 10 <sup>-2</sup>	+0,61	> +1,8*)	+0,25*)
Cr	4 · 10 <sup>-3</sup>	-0,25	+1,2	-0,71**)
AKVS I	2 · 10 <sup>-4</sup>	+0,06	+1,2	-

\*) Podle Latimera. — \*\*) Pro rovnováhu Cr/Cr<sup>3+</sup>.

Key to Table 1. 1) Review of Passivation Potential and Critical Passivation Currents for Certain Metals in 1 N H<sub>2</sub>SO<sub>4</sub>. Potentials in Hydrogen; 2) Material; 3) Critical Passivation Current a/cm<sup>2</sup>; 4) Passivation Potential V; 5) Transpassivation Potential V; 6) Standard Potential V; 7) \*) according to Latimer - \*\*) for Cr/Cr<sup>3+</sup> equilibrium.

The passivation potentials of iron and nickel are substantially higher. Also further oxidation potentials are likewise staggered; about transpassivation we speak as a rule only in case of Cr, because the very same effect may originate in it also. In Fe and Ni oxygen begins separating even before the attainment of this potential (Figure 1).

Values of passivation and transpassivation potentials depend also upon the pH of the medium. M. J. N. Roubaix<sup>3)</sup> devoted much time to this problem.

To bring the metal onto the necessary passivation potential, it is necessary to polarize same with variable critical passivation current. The magnitude of the critical passivation current depends on the properties of the given metal, on the solubility of the reaction product in the given medium and on the rate of its transportation from the anode. If the removal of the anodic reaction products is not fast enough, i. e., the metal ions, stages of their concentration at the surface of the electrode are so that it will exceed the limit of solubility of the metal salt or hydroxide. In this moment a primary passive layer of hydroxide will form, which will limit the extinction of the ion at the surface of the electrode. Under this layer conditions are created for the origination of the natural passive oxide layer. In media, where primarily originating metal hydroxide is practically insoluble, the critical passivation current is very small. This case is valid for example, for a majority of metals in a neutral or moderately alkaline medium (see Figure 8), until a certain complex forming effect is not included. In media, where the primary reaction product is well soluble (e. g.,  $(OH)_2$  in  $H_2SO_4$ ) the critical passivation current can be much higher. Its magnitude depends nevertheless upon other circumstances, especially when they have an effect on the rate of removing the reaction product from the surface of the electrode, i. e., on diffusion and convection.

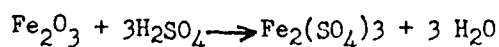
In Table 1 the values of the critical passivation current are compared for the mentioned three components of stainless steel. For Cr this value is the lowest, which gives further proof of its tendency toward passivation.

### III. Mechanism of Destruction of Passive Layer

It has already been mentioned, that the passive state of the metal without further additional oxidation is unstable. The passive oxide layer in aggressive media is upset sooner or later, before the free metal surface is revealed, i. e., before the electrode is activated. The upsetting takes place basically by two mechanisms:

(metal ion)

A. The passive oxide layer is upset by the solution, the valence of the ion/is changed in the oxygen, consequently:



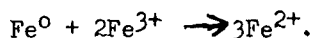
Trioxides of iron, chromium and nickel, which originate in passive layers, are even in strong oxygens highly resistant and less soluble, just as the very same oxides in pure crystalline form.

B. The passive layer is upset by the reduction in the ternary component (trivalent component)? of the oxide layer and secondary dilution of the bivalent oxide, The rate of this action is controlled by the rate of reduction, because the dissolution of divalent oxide can already be very rapid. The reduction of stable trivalent oxide into unstable divalent may take place repeatedly in several days:

1. Chemical: in the presence of a reducing agent in the solution, i. e., in the solution with low redox potential;

2. Electrochemically: by the cathodic polarization of the electrode. Reduction mechanism according to 1 and 2, is the same, i. e., the electrodes are shifted into sufficiently negative potential (activation).

3. Reduction in permanent condition. The metal ion atoms of the own electrode, diffuses the passive oxide layer thus reducing same, which is evident from the schematic reaction:



The rate of this diffusion depends upon the ion and electron conductance of the passive layer as a semiconductor. Oxides of iron and nickel are extremely good conductor so that their reduction can be rapid (Figure 3). Chromic oxide reacts and its layer has especially good protective properties.

Diffusion of the metal ion atom by oxide takes place under normal temperatures at a very slow rate, at a slightly thick passive layer the stream of the diffused metal is measurable just like an electrochemical stream.<sup>4)</sup>

An effective composition and state of passive layer is so far not known. Trivalent oxides can be used here with their own crystalline lattice or in form of

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spinel, which are best suitable by their chemical stability. Even more complex ratios can be expected in mixed oxides originating on alloys. A more detailed study of a semiconductor may bring new ideas into investigating the properties of such layers. For example, small changes in the composition of a semiconductor may substantially change its electric and also in this connection its chemical properties<sup>5)</sup>.

A combination of solution and reduction of the layer represents then a definite rate of upsetting the passive layer toward active state. This rate can be expressed by an equivalent electric current, with which the passive metal has to be additionally oxidized as to replenish the disrupted passive layer and the metal should remain in passive state. The appropriate consumed current can be a measure of metal corrosion in passive state. The rate of corrosion in passive state is generally considerably lower than in active state; for example, in iron in 1 N  $H_2SO_4$  this ratio has a value of perhaps 1:10<sup>5</sup>.

C. The passive layer is disrupted by oxidation of a trivalent component of an oxide layer into a much higher soluble form. Such a reaction may be chemical or electrochemical, analogous as in B.

In passive state corrosion depends first of all on the properties of the passive layer. The corrosive medium affects the stability of the passive state and this

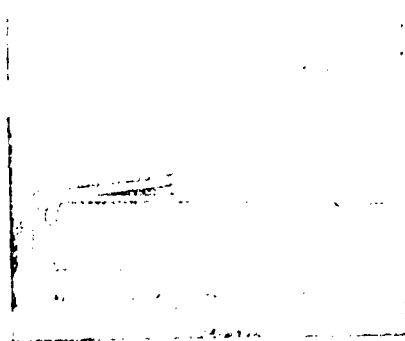


Figure 3. Anodic Polarization Curve for Ni in 1 N  $H_2SO_4$  with Passivation and the activation Process.

At a constant increase in current density Ni dissolves anodically with rising polarization. After exceeding the critical passivation current at  $5 \cdot 10^{-2} \text{ a/cm}^2$  there is sudden passivation and rise in potential; on the electrode oxygen is separated. After cutting off the current in point  $I = 0$  the dependence of the potential of the passive electrode upon time is registered. The first jump of the potential to negative values is due to the switching over the oxygen separation; further arbitrary drop in potential is due to gradual reduction of the oxide layer by Ni diffusion. After reduction, the layer dissolves and the potential drops by an activating jump to the initial value of the active Ni.

effect unites with the effect on the stability of the value forming the passive layer. The natural metal material is maintained, with exception of the fact that the formation of the passive layer has participated, thus affecting further corrosion but to a lesser extent.

#### IV. The Mechanism of Chemical Passivation

All the passivation effect described so far have been investigated and they controlled outer polarization of metal electrodes. As we will be shown further on, it is possible to change outer polarization of electrode by submerging same into the solution or real oxidizing or reducing properties present in a real redox potential. The findings acquired by electrochemical methods will be applied also for the actions taking place as a purely chemical reaction.

Each aqueous medium is designated by a definite redox potential, to it should be applied the forced immersion of an electrically conductive electrode. As long as the electrode is immersed inertially (on e.g. platinum), the proper redox potential of the given medium will be established on it. But as long as the immersed electrode reacts with the solution and makes the effort of attaining the given potential, different from the redox potential of the solution, there is mutual polarization of both systems. For example, pure iron immersed in 1 N raw acid without oxygen acquires here a potential of perhaps -0.32 v, whereby there is practically no reaction. If the solution becomes saturated with atmospheric oxygen, it behaves as a redox of the system with the redox of the potential of perhaps + 0.95 V<sup>\*)</sup>. Iron immersed in this acid acquires a mixed potential - 0.24 V whereby the metal becomes oxidized and the redox of the system is reduced, in this case of the dissolved oxygen.

On the reduction polarization curve of the oxygen dissolved in acid (Figure 4) it can be found, that the reaction takes place at half wave potential + 0.70 V and attains a limited current of perhaps  $1.2 \cdot 10^{-4}$  a/cm<sup>2</sup>, provided the solution is

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\*) This value was measured on Pt and is attributed to the presence of PtO<sub>2</sub>. The theoretical value is lower.

saturated with air and is at a standstill. At this rate oxygen is reduced to a potential in the neighborhood of about 0.0 V; at more negative values of the potentials there is separation of the hydrogen and a rise in current. If the iron electrode in acid with oxygen has a potential of - 0.24 V, the fact is characteristic that the reduction of the oxygen does not take place at proper rate (roughly limited), as can be surmised from Figure 4. There is still no hydrogen separation here with respect to its switching over on the iron. At the very same rate, i. e., equivalent rate, the iron does transform into solution which can be confirmed experimentally.

The high redox potential of the solution saturated with atmospheric oxygen should be sufficient for the passivation of Cr, Fe and Ni because it lies in the passivation zone of all three metals (Table 1). We have already found that the high redox of the potential is absolutely necessary but not a sufficient condition for chemical passivation of the metal<sup>6)</sup>.

As was mentioned before, to passivate the metal in the given condition, it is necessary to attain real critical passivation current densities. Oxygen dissolved in solution may nevertheless oxidize metal (and in itself become reduced) but at an extremely slow rate which corresponds to a current density considerably lower than ( $0.12 \text{ ma/cm}^2$ ) which is necessary for the passivation, for example of iron ( $600 \text{ ma/cm}^2$ ). Only highly concentrated oxidation agents (e. g., concentrated  $\text{HNO}_3$ ) can react so rapidly as to be able to passivate iron in an acid medium. The case with Cr and its alloys is entirely different, which is characterized by low passivating current density and can be passivated by the effect of less concentrated oxidation agents. Also, iron passivates easily in an alkaline medium where its critical passivation current density is very low.

In perfect agreement is the description of the mechanism for autopassivation of metal in oxidizing media given by V. P. Batrakov<sup>7)</sup>. In contrast to our remarks, the consideration of the cathodic and anodic processes is always individually here, i.e.,

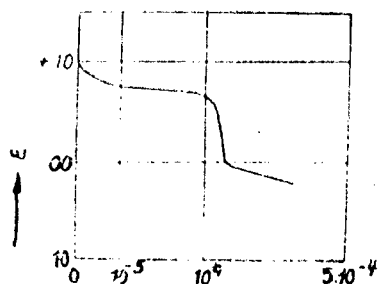


Figure 4. Polarization Curve of Atmospheric Oxygen Reduction in 1 N  $H_2SO_4$  on Flat Platinum Electrodes.

Stages of current densities with reference to their squares.

as taking place on different microelectrodes.

#### V. Passivation Diagram

These relations will be depicted by a quantitative diagram, similar to the Evans corrosion diagram. In contrast to this, we do not consider separately the effect of anode and cathode, but we consider the anodic and cathodic reaction on one surface of the metal electrode. These remarks are valid also for a purely chemical reaction, for chemical passivation and for chemical homogeneous corrosion.

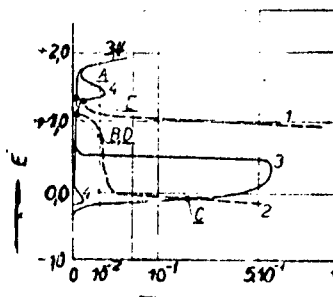


Figure 5. Passivation Diagram for Iron and Stainless Steel in Concentrated and in 5 M  $HNO_3$ .

Polarization curves of the metal were derived as a dependence of the current upon the potential; the stages of current densities are plotted in the other squares. 1) part of cathodic polarization of the curve content,  $HNO_3$ ; 2) cathodic polarization curve 5 N  $HNO_3$ ; 3) polarization curve of iron; 4) polarization curve of stainless steel (both in 1 N  $H_2SO_4$ ). Current values in active zone are enlarged by 10X. Meaning of point: A. stable passivation of Fe in concentration  $HNO_3$ ; B. labile passivation of Fe in 5M  $HNO_3$ ; C. corrosion of activated Fe in 5M  $HNO_3$ ; D. stable passivation of stainless steel in 5 M  $HNO_3$ ; E. corrosion of stainless steel in transpassive state in concentr.  $HNO_3$ .

On the diagram, Figure 5, anodic polarization curves are plotted for metal material (iron and steel 18-8) and cathodic polarization curves of the appropriate medium (concentr.  $HNO_3$  and 5M  $HNO_3$ ). The intersection of anodic and cathodic curves

offers the condition that the system is situated in it. From the position of the intersection, it is evident that iron is passivated only by concentrated acid (intersection in the passive zone of the iron). In 5 M  $\text{HNO}_3$  iron cannot actively passivate but dissolves at a rate of perhaps 350  $\text{ma/cm}^2$ . Since at such conditions, hydrogen begins separating (hydrogen depolarization), the rate of corrosion depends greatly upon the overvoltage of the hydrogen and purity of the used iron.

Stainless steel when its critical passivation current density is considerably lower, passivates more smoothly in diluted  $\text{HNO}_3$ , as is shown by the intersection of both curves. For the passivation of stainless steel, it is sufficient to dissolve air in acid. According to the curve (see also Figure 6) on passive stainless steel at progressing potential, there is never separation of oxygen (as on iron), but at a transpassivation potential ( + 1.2 V in 1 N  $\text{H}_2\text{SO}_4$  ) it comes to oxidation of the chromite component of the passive layer on dissolved chromium ions.

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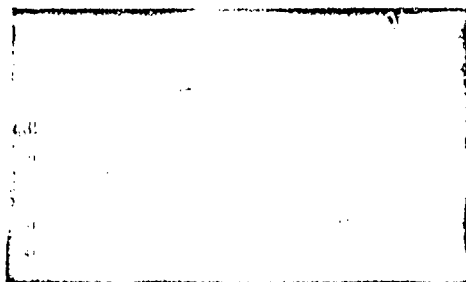


Figure 6. Potential Polarization Curve of Stainless Steel in 1 N  $\text{H}_2\text{SO}_4$ .

Before oxygen separation in transpassive zone corrosion current is reduced.

That is why immersion of chromium steel into solution with high redox potential (e. g., concentr. of  $\text{HNO}_3$  especially under heat) jeopardizes these corrosion materials in the transpassivation zone. Rate of corrosion in transpassive state is also limited by the real maximum value (expressed by equivalent current density) as is evident from the diagram. The more Cr contained in the alloy, the faster the corrosion can be in transpassive state as we have observed on samples with various Cr content.

For corrosion is also important, as to whether the metal, already in passive state, will be able to maintain its passivity in the given medium. It is evident that, in a medium where passivation does take place, this condition is stable.



There are however cases where, in the given medium, will not suffice or the given material will not be able to passivate, but is capable of maintaining same in passive state, by another originated composition (e. g., oxidation in open air). In this case we speak about labile passivation. This phenomenon can be explained by the fact that to maintain passive state it is sufficient to have a considerably lower current density (corrosion equivalent in passive state) in comparison with critical passivation current densities. The potential of the passive metal and also the redox potential of the solution should of course not drop to below the value of the activation potential for given metal and medium. This phenomenon is known for example, in iron, to maintain its passive state  $\text{HNO}_3$  of lesser concentration than the one necessary for passivation, is sufficient.

On the diagram the labile passive state is characterized by the existence of two intersections of polarization curves, one of which lies in the passivation zone and the other one in the activation zone of the metal. It is conceivable, that to use the material as a condition, when it is in labile passive state, is kind of risky. It will come for some transient reason to activation and without outer help, the metal cannot return into passive state and it is threatened by higher corrosion.

E. Houdremont<sup>8)</sup> considered as labile, passive steel with a Cr content of perhaps 12 to 16%. According to our ideas, this applies only to a medium, the passivation of which is capable to give the presence of atmospheric oxygen. In a medium with higher oxidation capabilities, these steels can be stably passive.

In cases of labile stability, it is convenient to employ so-called anodic protection of the metal material. The outer source of electric current (or voltage) safely retains the protected metal on a potential in passive zone<sup>9,10)</sup>.

#### VI. Effect of Material Structure

The mentioned remarks about chemical passivation of steel and metal pertain to homogeneous material and is, therefore, valid only for one phase of the investigated material (alloy). In a great number of instances this single phase represents the

main difference between the alloy and the mentioned ratios, but they are nevertheless in agreement with the effective corrosion behavior. Wherever we find the separation of other phases of substantially different properties (especially less noble) they are threatened by faster corrosion disruption and dangerous heterogeneous corrosion, e. g., intercrystalline corrosion. In such cases the generally real process of alloy corrosion may deviate considerable from the simple ratios. These ratios, which deserve thorough investigation regardless of the scope of operation.

#### VII. Experimental Part

Polarization curves, needed as the bases for studying the mentioned electric reactions were obtained however, as a dependence of the potential upon the current, in part as a function of inversion, i. e., dependence of current on the potential applied to the electrode.

Polarization curves corresponding to the applied current were acquired by electronic equipment with automatically rising polarization current and with photographic registration of curve from the picture screen of the electron oscillograph. This method was described in detail in a separate report<sup>11)</sup>. Its convenience lies first of all, in addition to the rate, in the improvement of reproducibility of measured curves relative to the better controlled time dependences of the measured potentials. In this way there was established a critical passivation current density of the metal and limiting reduction currents for the redox system.

Polarization curves corresponding to the applied potential were obtained by electronic controlling potentiostat; a more detailed description of same is given somewhat later. The automatic device, and with minimum delay, controls the current passing through the investigated electrode by such a value, that the electrode should retain the selected potential with respect to the nonpolarized reference electrode, which is provided with a capillary probe closely fitted to the surface of the investigated electrode. In this arrangement regardless of the potential of the auxiliary polarization electrodes and upon the potential drop in the electrolyte,

the effective inner resistance of the entire measuring circuit is sufficiently low, perhaps  $0.3 \Omega$ .

The block diagram of the controlling potentiostat is shown in Figure 7. The potential of the reference electrode RE, relative to the grounded electrode  $E_1$ , is amplified by a DC amplifier ZES, after applying the control voltage from the REG potentiometer, and is guided to the control grid of the operating final electron tube KP. In order that such an electronic tube should work amidst its own characteristics, its unperturbed anode current was compensated by a constant current from the GK current.

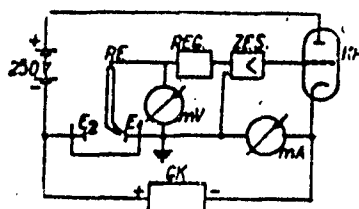


Figure 7. Block Diagram of the Control Potentiostat.

$E_1$  - measured electrode;  $E_2$  - auxiliary electrode; RE - reference electrode; REG - potential regulation; ZES - DC amplifier; KP - end performance pentode; GK - DC current generator.

The potential of the investigated electrode and the passing current are measured in designated points, by a tube millivoltmeter and milliamperemeter, and is entirely of the internal resistance.

Both values can also be measured simultaneously by an oscillograph.

Curves obtained in such a manner were used in compiling the polarization diagram. The accuracy of measuring the potential was  $\pm 5$  mv; the reproducibility of the measured potentials was in a majority lower. In the text potentials are listed in hydrogen stage; in the oscillograms they are referred to as the SKE Potentials.

Experimental electrodes were prepared from technically cast pure metal to a substance for casting the polished piece (Dentakryl), to which an electric wire was already connected. As a sample of the steel 15% Cr, 8% Ni stabilized with Ti, AKVSI material was used. The geometric area of the sample was selected with view of the necessary current density in size of  $5 \text{ mm}^2$  to  $1.2 \text{ cm}^2$ . The surface of the sample was polished with Corundum No. 600. The surface of the electrode was suspended into

into the solution; the solution was not mixed, so that there was only inherent convection of the electrolyte.

All was measured together in 1 N  $\text{H}_2\text{SO}_4$  at temperatures of  $24 \pm 2^\circ\text{C}$ .

#### VIII. Discussion of Results

From the mentioned viewpoints, corrosion resistance is inherent of standard stainless steel (18-8) and is indicated first of all by the presence of Cr, which with an increasing concentr critically decreases the passivation current of the given alloy. Its presence also decreases the passivation potential. To passivate Cr and its alloys, it is sufficient for these reasons to have a medium with weaker oxidation capabilities (i. e., lower redox potential with lower limiting reduction current, corresponding to lesser concentration of oxidizing components) than is needed for example in case of Fe. In ordinary corrosion media, these steels can passivate under the effect of dissolved atmospheric oxygen.

The presence of Ni is reflected by a further reduction in critical passivation current by a value of perhaps  $0.2 \text{ ma/cm}^2$  (in 1 N  $\text{H}_2\text{SO}_4$ ). This further raises the tendency of stainless steel toward passivation and reduces the rate of corrosion in active state. Also in transpassive state Ni reduces the maximum rate of corrosion; but on the magnitude of the transpassivation potential it has no important effect.

Because stainless steel is corrosion resistant by its passivation, it also has conditions which are hazardous, leading toward activation, i. e., disruption in the protective layer. Activation may take place for several reasons:

A. By the effect of highly aggressive medium which attacks even highly passive layers containing  $\text{Cr}_2\text{O}_3$ , e. g., on boiling acids. If the examined material has to resist such a medium, it is necessary to select its composition so, that the appropriate passive oxide layer on this material should be sufficiently resistant. We as a rule have a steel with a higher Cr content. It is also necessary to point out that the material will remain in passive state (with an anodic protection).

B. The effect of the reduction medium may reach a reduction in passive layer

and to its easier destruction. Solutions with a redox potential lower than the activation potential of Cr (steel 18-8), although they can activate, are quite infrequent. To the potential in the activation zone, there can be brought the investigated material when combined with a highly refined metal, e. g., zinc.

GRAPHIC NOT REPRODUCIBLE

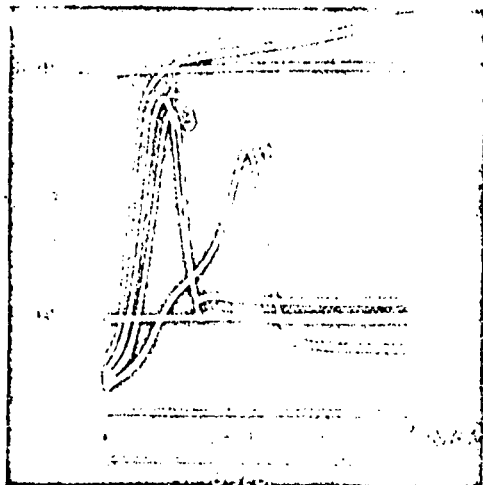


Figure 8. Disturbing Effects of Chloride Ions on the Passivation of Iron.

Anodic polarization curves of Fe in a 0.1 M  $\text{NaHCO}_3$  solution with various NaCl content, w/o chloride; 2 - 0.05 M NaCl; 3 - 0.1 M NaCl; the electrode passivates at the first and the potential rises rapidly. At the moment of reaching the passive layer destruction by the effect of Cl-ion the potential drops rapidly and the electrode dissolves with small polarization. It is also evident from the drawing that for the passivation of Fe in a moderately alkaline medium is sufficient for a low current density.

The passing of the electric current leads to activation of the stainless steel, it will in this way become a cathode and reduce the passive layer. With proper construction of the equipment, it will be possible to cut out a majority of these possibilities for activation and preserved and the material so used against a rise in corrosion.

C. Disruption of the passive layer may be brought by the presence of certain ions in the corrosion medium. A row of ions - particularly Cl - ions - has the ability to disrupt the passive layer on metals. Passive Fe and Ni layers are especially sensitive (Figure 8); layers containing a sufficient

amount of Cr are somehow more resistant to Cl - ions. Consequently, steel with a 50% Cr content is sufficiently resistant in a medium containing Cl-ions, as was remarked by Houdremont. But this resistance cannot be placed as a primary continuity with resistance against oxidation agents. According to our measurements on the other hand, we can state that with an increasing Cr content (up to 100%) corrosion in transpassive state can be much faster. The higher resistance to Cl-ion

is imparted to the steels by the presence of other alloyed elements (e. g., Mo).

D. Oxidation of the chromite component of a passive layer and to corrosion in passive state may come under the effect of highly oxidizing medium. With respect to this reaction, stainless steels are attacked by solutions with high redox potential. Identically may be the effect of electric current passing, the steel will become an anode.

#### IX. Conclusions

With the method of potential polarization it is very easily possible to establish on stainless steel and on other metal materials certain values characteristic for the corrosion behavior of the appurtenant materials (passivation and transpassivation potential, critical passivation current, corrosion current in passive state, etc.). On the basis of these data it is possible to determine the conditions quite accurately, by which it is possible to investigate a material for its corrosion resistance (particularly in passive state). By comparing the electrochemical behavior of the metal material and the corrosive medium, by studying the polarization curves in the passive diagram, it is easy to guess the corrosion behavior of such a system.

With the aid of a metallographic microscope, it is easy by this method to study the specificity and the behavior of such phases in an alloy, percentage-wise its multiplicity is very small, and its behavior cannot be affected by the presence of the remaining phases, as is the fact in experimental methods without an accurately controlled potential.

We assume, that on the basis of these theoretical ratios and with the aid of the employed measuring methods, the development of new species of alloyed metals with the viewpoint of corrosion resistance will be facilitated, that a closer stage of intercrystalline corrosion of stainless steel will be made possible and that it will be possible to obtain more accurate bases for the application of anodic protection on stainless steel.

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